



Synergistic effect in plasmonic Au/Ag alloy NPs co-coated TiO₂ NWs toward visible-light enhanced CO₂ photoreduction to fuels



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ABSTRACT

Plasmonic Au/Ag alloy NPs supported on TiO₂ nanowires (TiO₂ NWs) have been designed and synthesized through a facile hydrothermal and photo-deposition method. The samples were characterized by XRD, FE-SEM, TEM, N₂-adsorption-desorption, XPS, Raman, UV-vis and PL spectroscopy. Bimetallic Au/Ag NPs were presented over the TiO₂ NWs as an alloy, thus exhibited strong absorption of visible light due to the localized surface plasmon resonance (LSPR) excitation. The synergistic effect in plasmonic Au/Ag alloy NPs for selective photocatalytic CO₂ reduction with H₂ to CO and hydrocarbons under visible light irradiation was investigated. The present design of plasmonic Au/Ag NPs co-decorated TiO₂ NWs leads to remarkably enhanced photoactivity of CO₂ reduction to CO. The CO evolution rate as a main product over the Au-Ag alloy NPs coated TiO₂ NWs was 1813 $\mu\text{mole-g-catal.}^{-1} \text{h}^{-1}$ at selectivity 98%. This amount was approximately 1.72 time larger comparing to Au-NPs/TiO₂ NWs, 1.84 fold more than the Ag-NPs/TiO₂ NWs, 72.52 fold than the TiO₂ NWs and 201 fold more than the amount of CO produced over the bare TiO₂-NPs. This great enhancement can be attributed to synergistic effects in Au/Ag-NPs, enhanced visible light absorption due to Au-Ag alloy formation and improved charge separation in LSPR-excited TiO₂ NWs. In addition, turnover productivity is introduced to investigate the effect of operating parameters on the performance of photocatalysts. The plasmonic reaction mechanism of Au-Ag NPs in conjunction with LSPR excitation and charge transport to understand the reaction pathway is described.

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1. Introduction

Transformation of CO₂ to more value added chemicals is a promising carbon management approach to offset the cost of implementing CO₂ capturing technologies. Among the other alternatives, solar photocatalytic conversion of CO₂ appears the most prospective path, since it would be helpful to lessen atmospheric CO₂ level and can partly achieve energy demands [1–3]. The most of the work in photocatalytic CO₂ reduction has been related to using water as a reducing agent. Generally, the main products during the photo-induced CO₂ and H₂O reactions are CO and CH₄ using the gas phase photoreactor system [4–6], but the formation of CH₃OH has also been reported [7]. However, H₂O is hardly reducible and yielded lower CO₂ conversion efficiency and products selectivity [8]. Recently, reduction of CO₂ by H₂ to CO via photocat-

alytic reverse water gas shift (PRWGS) reaction has been the most attractive approach in CO₂ conversion applications [9,10].

Since the discovery of photocatalytic CO₂ reduction over the semiconductor materials, TiO₂ is one of the most widely used and promising photocatalyst because of its high activity, low-cost, non-toxicity, abundantly availability and chemically inertness [11,12]. However, the efficiency of the pure TiO₂ is low owing to fast recombination of photo-generated charges [13]. Besides, TiO₂ is functional only under ultraviolet (UV) light because of wide band gap energy (3.20 eV for anatase phase and ~3.0 eV for rutile phase). Recently, TiO₂ nanomaterials such as nanosheets, nanowires, nanorods and nanotubes are considered as the superior candidates in photocatalysis applications. These materials have distinctive physical and optical properties, thus offer a direct pathway for efficiently collecting photons and/or electrons. The one dimensional (1D) nanomaterials with regular structure can provide large surface area, thus enriched photo-generated charges transport and have hindered charges recombination rate [14–16]. Therefore, development of a photocatalytic system based on structured TiO₂ that could utilize solar energy is important for practical applications.

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Many approaches to develop solar active TiO₂ nanomaterials including doping and photosensitization have been suggested by many researchers. Metal-doping is one the most favorable approach for narrowing the band gap energy, while metal-doped ions in TiO₂ act as a barrier and prevented photo-excited electrons and holes recombination. Noble metal nanoparticles such as gold nanoparticles (Au-NPs) and silver nanoparticles (Ag-NPs) have been successfully reported as photosensitizers to improve TiO₂ photocatalytic efficiency under visible light [17,18]. These metals have strong absorption of visible light based on their characteristics of localized surface plasmon resonance (LSPR). In LSPR-excitation, light energy can be coupled into metal NPs and plasmon-induced electrons can be injected to semiconductor to make it visible light active [19]. Moreover, noble metal NPs possess electron storage properties, resulting in improved electron-hole pair separation in metal-semiconductor composite system [20].

During the last years, a number of reports relating to photocatalytic activity of LSPR induced TiO₂ and its mechanism under visible light irradiation has been presented [21–24]. LSPR induced TiO₂ by Au-NPs have been reported by many researchers [25–28]. The photo-deposited Au-NPs onto TiO₂ for CO₂ reduction to hydrocarbons have proven significant effect on the photocatalytic activity and products selectivity [29]. Photocatalytic CO₂ reduction to CH₄ over macro-porous TiO₂-supported Au-NPs has been reported with improved photoactivity due Au-NPs LSPR effects [30]. When, Au/Pt NPs decorated TiO₂ nanofibers were used for photocatalytic H₂ production and CO₂ reduction, Au-NPs facilitated for visible light absorption through the LSPR effect, while Pt served as an electrons sink to retard the charges recombination rate [22]. Recently, we investigated Au-NPs-promoted TiO₂ nanowires for selective photocatalytic CO₂ reduction to CO. Significantly improved TiO₂ activity under visible light was observed by LSPR effect of Au-NPs [31]. On the other hand, Ag-NPs have been also proven to give strong visible light absorption based on the LSPR [32,33]. Liu et al. [34] reported photocatalytic CO₂ reduction with H₂O to CH₃OH over plasmonic Ag/TiO₂ NWs under visible light. The improved TiO₂ photoactivity for CH₃OH production was observed due to Ag-NPs LSPR effect.

So far most of the previously reported Au and Ag based TiO₂ composites have been prepared using spherical TiO₂ nanoparticles with single metal loading. Only limited reports demonstrate LSPR driven CO₂ reduction over plasmon-induced TiO₂ under visible light. Au/Ag NPs loaded rutile TiO₂ photocatalyst has been investigated for photo-decomposition of 2-propanol. The photocatalytic activity was significantly enhanced due to electron injection from LSPR excited Au/Ag NPs into TiO₂ under visible light [35]. Recently, the synergistic effect in Ag-In electro-catalysts for CO₂ reduction has been demonstrated with enhanced photoactivity and selectivity [36]. Furthermore, the wavelength tuning of LSPR system can be achieved by modifying the size, shape and type of noble metals loaded over the TiO₂ surface. In this perspective, a promising approach is the use of Au-Ag alloy, which can absorb visible light over a broad range of solar spectrum. Verbruggen et al. [37] synthesized Au-Ag alloy NPs supported on the TiO₂ and reported tunable visible light activity toward the degradation of stearic acid. Therefore, it is of great importance to explore synergistic effects in Au/Ag bimetallic nanoparticles supported on the TiO₂ NWs for visible light applications. The present research aimed to investigate synergetic effect in Au/Ag alloy NPs decorated on TiO₂ NWs for LSPR-induced CO₂ reaction by H₂ to provide a way to absorb visible light and could improve photoactivity for selective solar fuels.

Herein, we designed and synthesized Au-Ag bimetallic nanoparticles supported on TiO₂ NWs and discussed their synergetic effects for LSPR-excitation under visible light. Au-NPs loaded TiO₂ NWs were synthesized by a modified hydrothermal and a chemical reduction route, while the Ag-NPs were photo-deposited onto TiO₂ NWs. Au-Ag alloy was synthesized by a chemical reduction and

photo-deposition under UVA illumination. The structured nanocatalysts were investigated for plasmon-induced CO₂ reduction to CO and hydrocarbons using H₂ as a reductant. More importantly, the turn over productivity (TOP) analysis is introduced for systematic understanding the effect of operating parameters on the activity of photocatalysts. The photocatalytic reaction process in conjunction with LSPR is critically discussed to understand the synergistic effect in Au-Ag NPs toward CO₂ reduction.

2. Experimental

2.1. Synthesis of TiO₂ NWs

Initially, TiO₂ nanoparticles were synthesized through a simple and direct sol-gel method according to our previous work [4]. TiO₂ NWs were prepared using a facile hydrothermal synthesis technique as follows (refer to Fig. 1). First, 1 g TiO₂ NPs was suspended in 8 M NaOH solution (50 mL) and stirred for 10 min. The sample was then transferred into Teflon-lined continuous stirred reactor and heated to 110 °C under continuous stirring for 2 h before the mixture was cooled to room temperature. The obtained suspension of TiO₂ NWs was washed with deionized water to get pH below 9. Finally, crystals were washed with 0.1 M HCl and deionized water to ensure no residual ions left in the sample. After being dried at 80 °C for 12 h, the samples were calcined at 500 °C for 5 h before stored in airtight glass bottles.

2.2. Preparation of Au/Ag NPs loaded TiO₂ NWs

The deposition of gold and silver nanoparticles on the TiO₂ NWs was conducted with a chemical reduction and photo-deposition method. Au-NPs coated TiO₂ NWs were prepared by the procedure briefly described as follows (refer to Fig. 1). 0.50 g of TiO₂ NWs powder was dispersed in 50 mL of ethylene glycol and the mixture was heated to 160 °C in a continuous stirred tank reactor. A certain volume of 0.025 M AuCl₃ solution was injected rapidly into solution and stirred for 10 min at 160 °C before the mixture was cooled to room temperature. The solids were filtered and oven dried at 80 °C for 12 h. The different volumes of AuCl₃ solution were used to get Au loading of 0.1%, 0.3%, 0.5% and 0.7 wt.%, respectively. Similar procedure was used to prepare Ag-NPs supported over TiO₂ NWs. The different volumes of AgNO₃ solution were used to get Ag loading of 2, 3, 5 and 7 wt.%, respectively. Finally, solids of Au and Ag loaded TiO₂ NWs were calcined at 500 °C for 5 h under air flow.

2.3. Preparation of Au-Ag bimetallic nanoparticles supported TiO₂ NWs

The Au-Ag-NPs supported TiO₂ NWs were prepared through a chemical and photoreduction method. Briefly, 0.5 wt.% Au-NPs-loaded TiO₂ NWs were immersed in a certain volume of 0.025 M AgNO₃ solution under continuous stirring. The mixture was then irradiated under UV-light irradiation using 200 W Hg lamp of light intensity 150 mW cm⁻² at wavelength 252 nm for 10 min to get gray precipitations before being dried in an oven at 80 °C for 12 h. Finally, the samples were calcined at 500 °C for 5 h to get final Au/Ag co-loaded TiO₂ NWs. The different volumes of AgNO₃ solution were used to get Ag loading of 1, 2, 3 and 5 wt.%, respectively. The schematics for the fabrication of Au/Ag-NPs loaded TiO₂ NWs is depicted in Fig. 1.

2.4. Structure characterization

X-ray powder diffraction (XRD) was recorded on a Bruker D 8 advance diffractometer with Cu- K α radiation ($\lambda = 1.54 \text{ \AA}$, operated at 40 kV and 40 mA) to identify the phase structure and

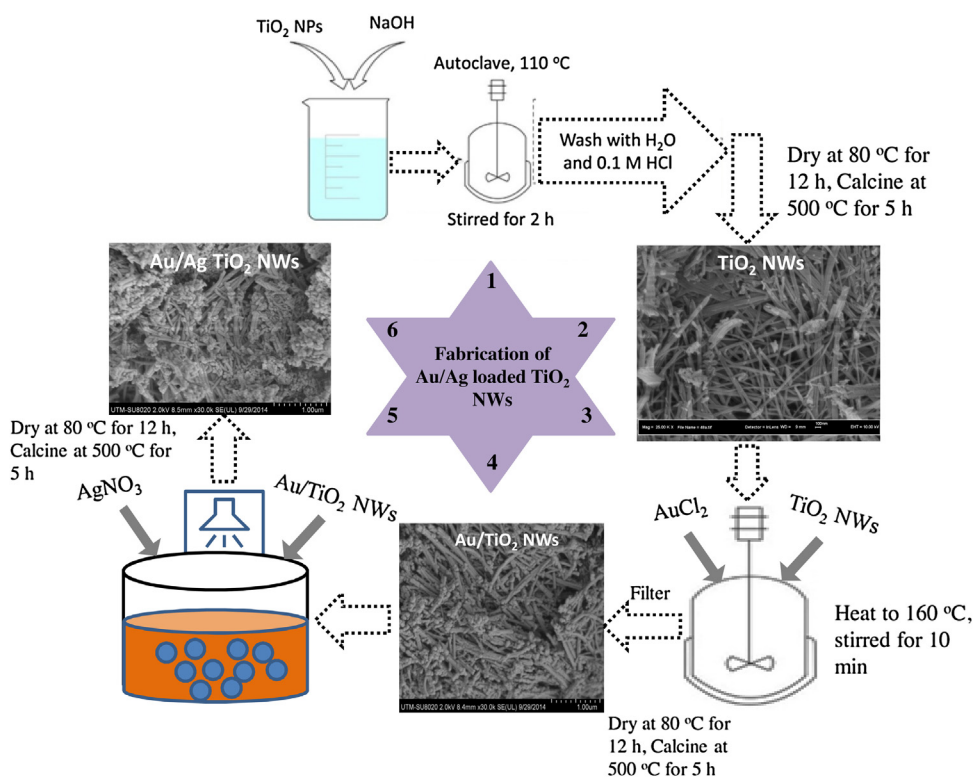


Fig. 1. Schematics for synthesis procedure of Au/Ag-NPs loaded TiO₂ nanowires.

phase transformation of all the samples. The morphology of the products was investigated using field-emission scanning electron microscopy (FE-SEM) with Carl Zeiss Supra 35 VP FE-SEM instrument. The transmission electron microscopy (TEM) was performed using JEOL-TEM apparatus operating with an acceleration voltage of 200 kV, which was used to measure the particle sizes and d-spacing of the samples. The XPS spectra were calibrated with respect to the binding energy of the C1s signal at 284.60 eV as an internal standard. Nitrogen-adsorption-desorption isotherms were collected using Micromeritics ASAP 2020 at 77 K. The samples were degassed at 523 K for 4 h under vacuum and by using the nitrogen flux. The Brunauer-Emmett-Teller (BET) surface area and pore diameters were calculated from the desorption branch of isotherms according to BJH method. Ultraviolet–visible (UV–vis) diffuse reflectance absorbance spectra were carried out on a Cary 100 Agilent UV–vis spectrophotometer equipped with an integrated sphere in the wavelength range of 200–800 nm. Raman and photoluminescence (PL) spectra of samples were recorded on a Raman Xplora Plus Spectrophotometer (HORIBA Scientific) with a 600 nm grating and a 532 nm emitting laser as an excitation source.

2.5. Photocatalytic testing and analysis

The photocatalytic CO₂ reduction with H₂ was carried out in a stainless steel rectangular reactor of total volume 108 cm³ [4]. A 35W HID Xe lamp was used as a visible light source with a light intensity of 20 mW cm^{−2} measured using a reference solar cell (91150 V, Newport). Similarly, a 200W Hg reflector lamp with a maximum light intensity of 150 mW cm^{−2} was used as a source of UV-light irradiation. The UV-light intensity was measured using an online optical process monitor ILT OPM-1D and a SED008/W sensor. The lamps were located at the top of the reactor equipped with a quartz window of 10 mm thickness for the passing of light irradiations. Typically, powder photo-catalyst (10 mg) was evenly dispersed inside the bottom surface of the reactor. Compressed CO₂

and H₂ (purity > 99.99%) regulated by mass flow controllers (MFC) were passed continuously through the reactor. The reactor pressure was maintained at 0.20 bars above the atmospheric pressure for the batch mode experiment by closing the outlet valves. The gas feed ratio of CO₂ and H₂ of 1 was used for all the experiments. The gaseous products were analyzed using an online gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with FID and TCD detectors (GC/FID/TCD). The FID detector was connected with HP PLOT Q column while the TCD detector consisted of HP Plot Q, Porapak Q, DC-200, UCW-982 and MS 13X columns.

The quantum yield (QY) was calculated to compare the performance of photocatalytic system with the previous researchers work. If one photon is used to generate one electron-hole pair, then the reaction quantum yield (QY) for CO₂ photoreduction is defined as the ratio of photons converted into electrons to produce specific product (mole per sec) to the total photonic flux (mole per sec) entering into the reactor as illustrated in Eq. (1) [38].

$$\text{Quantum Yield (QY, \%)} = \frac{n \times \text{moles of production rate (mol/sec)}}{\text{moles of photon flux (mol/sec)}} \times 100 \quad (1)$$

Where, n is the number of electrons required for the production of any specific product. In the specific case, 2, 6 and 8 electrons are needed for the production of CO, CH₃OH and CH₄. The moles of photon could be calculated from the visible-light input energy of intensity 20 mW cm^{−2}. Although, QY is an effective way to find photocatalytic system performance, yet this method is applicable at room temperature and atmospheric pressure and preferably used for slurry systems. In the case of gas phase system and in order to investigate the effects of process parameters such as catalyst loading, reactor volume, reactor pressure and temperature, the QY equation needed to be amended. Therefore, in this study, turn over productivity (TOP) is introduced to calculate the performance of the gas phase photocatalytic system as illustrated in Eq. (2).

$$\text{TOP (\%)} = \text{QY} \times \frac{PV}{nRT} \quad (2)$$

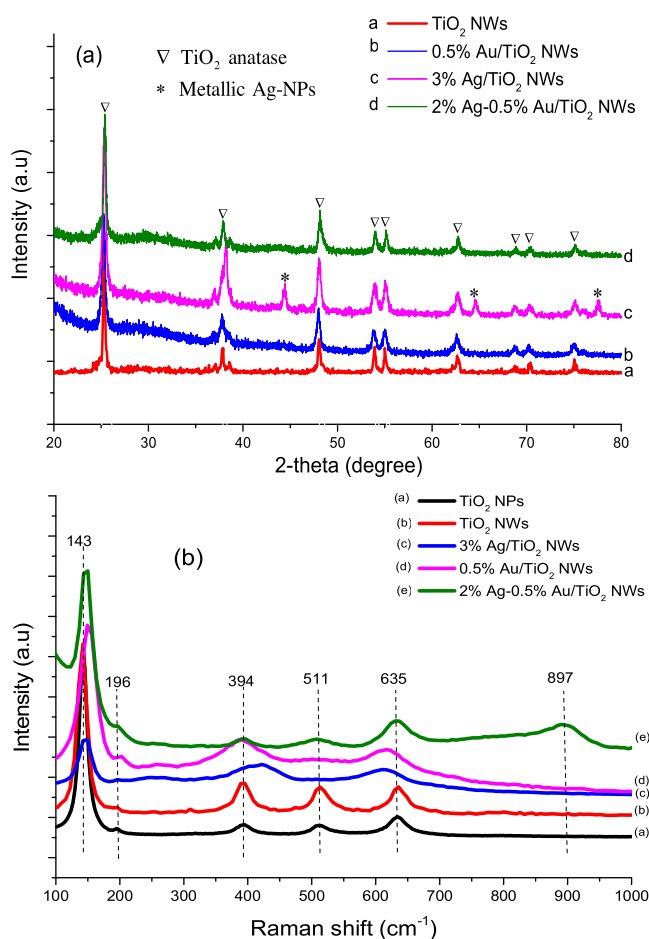


Fig. 2. (a) XRD patterns of different TiO₂ NWs loaded with Au/Ag nanoparticles; (b) Raman spectroscopy of TiO₂ NWs and Au/Ag loaded TiO₂ NWs.

Where, P is total reactor pressure, V is the reactor volume, n is moles of the catalyst used, T is the reaction temperature and R is the universal gas constant.

3. Results and discussion

3.1. Characterization analysis of nano-materials

All the prepared TiO₂ NWs and Au/Ag NPs loaded TiO₂ NWs were characterized by X-ray diffraction (XRD) and Raman to investigate the phase purity and crystallinity as shown in Fig. 2. The XRD patterns of the pure TiO₂ NWs and Au/Ag-NPs loaded TiO₂ NWs calcined at 500 °C for 5 h are shown in Fig. 2(a). The TiO₂ NWs and Au/Ag-NPs loaded TiO₂ NWs were in the pure anatase and crystalline phase of TiO₂. After modifying by Au/Ag nanoparticles, the diffraction peaks of TiO₂ NWs were unaltered. The spectrum of TiO₂ NWs with and without Au/Ag-NPs exhibits 2θ peaks located at 25.31°, 37.80°, 48.0°, 53.87°, 55.08°, 62.73°, 68.75°, 70.25° and 75.09°. All these peaks were consistent with (101), (004), (200), (105), (211), (204), (116), (220) and (215). This illustrates the presence of TiO₂ in anatase phase with growth axis in (101) directions when compared with JCPDS-ICSD standards for anatase (File No. 89-4921). However, Au-NPs peaks in Au-NPs/TiO₂ NWs were not detected to give any indication of the presence due to lower Au-contents.

On the other hand, the Ag-NPs peaks in the XRD pattern of Ag-NPs/TiO₂ NWs were detected at $2\theta = 44.35^\circ$, 64.65° and 77.62° , consistent with (200), (220) and (311). This observation matches

with JCPDS File No. 04-0783 and reflects metallic structure of the silver nanoparticles. More prominently, the peaks of Au/Ag NPs co-coated over the TiO₂ NWs were not detected, suggesting that Au and Ag species were combined together due to the formation of Au-Ag alloy and were probably due to the lower metal contents. Numerous reports have discussed the incorporation of metals and similar observations have been reported [39].

Fig. 2(b) presents the Raman spectrum of the pure TiO₂, TiO₂ NWs and Au/Ag modified TiO₂ NWs samples. The observed peaks in the Raman spectrum of the TiO₂ samples are relatively sharp and stronger than the Au/Ag NPs loaded TiO₂ NWs samples. In the case of pure TiO₂ samples, the intense Raman signals with E_{g(1)} mode appeared at 143 cm⁻¹ followed by low intense modes E_{g(2)} and E_{g(3)} located at 196 cm⁻¹ and 635 cm⁻¹, respectively. B_{1g} peak appeared at 394 cm⁻¹ and (A_{1g} + B_{1g}) reflected as a single merged peak at 511 cm⁻¹. All these peaks reveal the characteristics of the pure anatase phase of TiO₂. The Raman vibrational modes are evidently due to the bending vibration of Ti–O–Ti bond. However, the intense E_{g(1)} peak is related to O–Ti–O bending type, wherein only Ti moves and the oxygen movement remains fixed. In the case of (A_{1g} + B_{1g}) vibration peak, it includes the movement of only oxygen atom with Ti remains fixed.

The Raman spectra of Au/Ag NPs loaded TiO₂ NWs samples are identical to that of the pure TiO₂ NWs, which clearly indicated that the TiO₂ retained its structure after incorporation of these metals. Au/Ag NPs related signals were not identified because of the relatively low concentrations and due to the weak Raman scattering of these metals [41]. However, changes are obvious in the position and width of the Au/Ag NPs modified TiO₂ peaks. With the loading of Au and Ag NPs, the Raman band E_{g(1)} is slightly shifted toward higher wavenumber, Raman band B_{1(g)} and E_{g(3)} was broadened but their intensities were reduced. This indicated that the interaction between Au/Ag NPs and TiO₂ NWs affected the Raman resonance of the TiO₂ [42]. On the other hand, (A_{1g} + B_{1g}) vibration peak disappeared in both Au and Ag loaded TiO₂ NWs samples, probably due to less movement of oxygen atom in the presence of these metals NPs over the TiO₂ NWs structure. Furthermore, Au-Ag co-coated TiO₂ NWs have the similar reflection as that of the pure TiO₂ NWs, confirming anatase phase of TiO₂. More importantly, a distinct peak appeared at 897 cm⁻¹ by the presence of Au-Ag co-metals in the TiO₂ NWs, probably due to the formation of Au-Ag alloy. These observations have confirmed successful deposition of the Au-Ag alloy over the TiO₂ surface without any phase transition.

Fig. 3 exhibits FESEM images and EDX analysis of the pure TiO₂ NWs and Au/Ag NPs loaded TiO₂ NWs. Fig. 3(a) depicts TiO₂ NWs are uniform in length and no bundles of wires were observed. The EDX analysis in Fig. 3(b) shows the presence of Ti and O elements in the TiO₂. Fig. 3(c) and (e) depicts the presence of Ag-NPs and Au-NPs over the TiO₂ NWs. It can be observed that Ag-NPs and Au-NPs are entirely distributed over the surface of TiO₂ NWs. The EDX analysis of Ag-NPs and Au-NPs is presented in Fig. 3(d) and (f), confirming the presence of Ag and Au metals over the TiO₂ surface. The Au-Ag NPs co-loading with uniform distribution could be seen in Fig. 3(g). The presence of both Ag and Au NPs can be observed in Fig. 3(h). Noticeably, both metals can be evenly spread over the TiO₂ surface using chemical reduction and photo-deposition method.

The deposition of Au/Ag NPs was further investigated using high resolution TEM as shown in Fig. 4. TEM images in Fig. 4(a) and (c) clearly show the uniform distribution of Au/Ag NPs over the TiO₂ NWs surface. The TiO₂ NWs detected are different sizes with diameters in the range of 17–70 nm. Fig. 4(b) displays the particle size distribution of Au/Ag NPs in the range of 3–100 nm with a mean value of 20 nm. The large size Au/Ag NPs coated over the TiO₂ NWs were observed due to Au-Ag alloy formation. However, the amounts of large size Au-Ag alloy NPs existing in the sample are less than the separated plasmonic Au and Ag NPs. More impor-

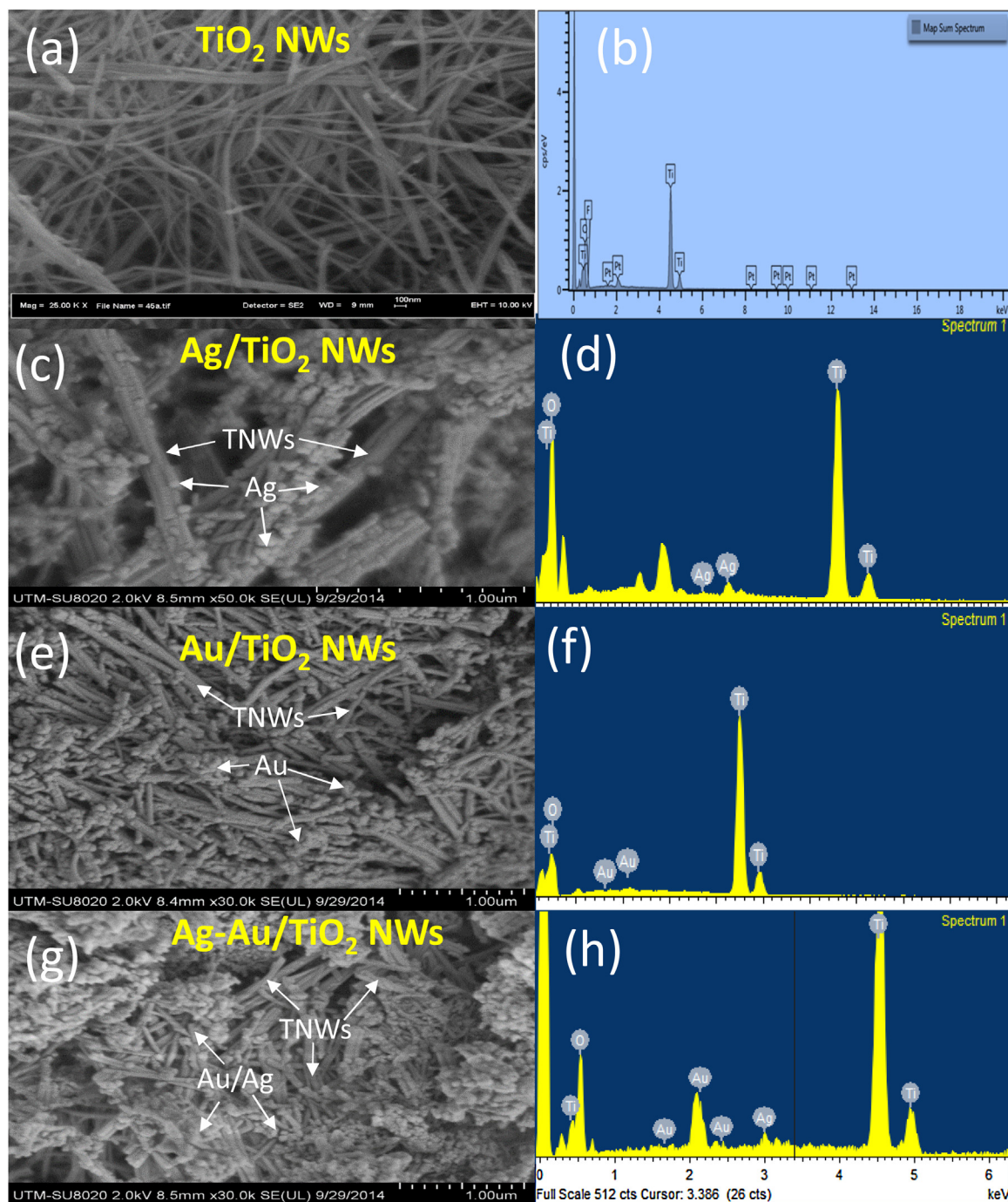


Fig. 3. FESEM images and EDX analysis of TiO₂ NWs and Au/Ag loaded TiO₂ NWs samples: (a) SEM image of TiO₂ NWs, (b) EDX analysis of TiO₂ NWs, (c) SEM image of Ag-NPs/TiO₂ NWs, (d) EDX analysis of Ag-NPs/TiO₂ NWs, (e) SEM image of Au-NPs/TiO₂ NWs, (f) EDX analysis of Au-NPs/TiO₂ NWs, (g) SEM image of Au-Ag NPs/TiO₂ NWs, (h) EDX analysis of Au-Ag NPs/TiO₂ NWs.

tantly, the smaller size Au and Ag NPs are also presented over the TiO₂ NWs surface which can serve as electrons sink to promote the charges separation. The HR-TEM was used to investigate the crystal structure of the Au/Ag NPs supported TiO₂ NWs, as shown in Fig. 4(d). The *d*-spacing of 0.35 nm reveals well the anatase TiO₂ (101) plane, as already investigated by XRD and Raman analysis.

The N₂-adsorption-desorption isotherms of the pure TiO₂, TiO₂ NWs and Au/Ag-NPs modified TiO₂ NWs samples are depicted in Fig. 5. The isotherms of all the samples are similar to the type IV curve with the hysteresis loops which is the characteristics of mesoporous materials. The summary of BET surface area, pore volume

and pore diameter of the TiO₂, TiO₂ NWs and modified TiO₂ NWs samples is depicted in Table 1. BET specific surface area (*S*_{BET}) of the pure TiO₂ was 42 increased to 75 m² g^{−1} for TiO₂ NWs. On the other hand, BET surface area decreased to 46 and 48 m² g^{−1} when 0.5 wt.% Au-NPs and 3 wt.% Ag-NPs were loaded onto TiO₂ NWs. This decreased in the BET surface area could be accounted for partial TiO₂ NWs surface covered by the deposited of metal NPs. However, an increased in BET surface area was observed in Au/Ag-NPs co-loaded TiO₂ NWs. This increased in BET surface area was evidently due to the Au-Ag alloy supported over the TiO₂ NWs. Similar observations were obtained in BJH adsorption pore volumes. In the case

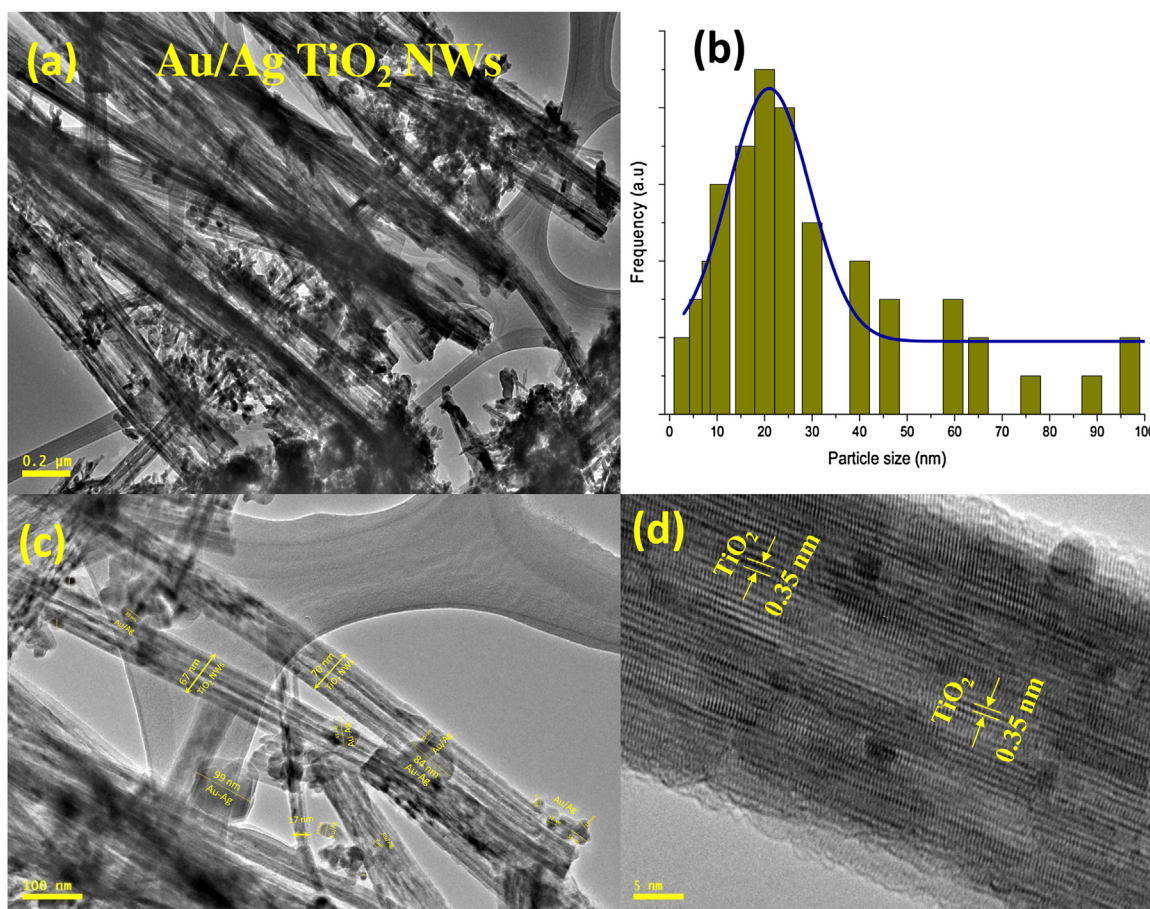


Fig. 4. TEM images of Au/Ag NPs supported TiO₂ NWs and their size distribution: (a and c) TEM images of Au/Ag-NPs/TiO₂ NWs at different magnification, (b) Au/Ag NPs size distribution over the TiO₂ NWs, (d) HR-TEM images with d-spacing of corresponding sample.

Table 1

Summary of physiochemical characteristics of TiO₂, TiO₂ NWs and Au/Ag-NPs modified TiO₂ NWs samples.

| Type of catalyst | BET surface area(m ² /g) | BJH adsorption pore volume(cm ³ /g) | BJH pore diameter(nm) | Band gap energy(eV) |
|------------------------------------|-------------------------------------|--|-----------------------|---------------------|
| TiO ₂ | 42 | 0.15 | 10 | 3.12 |
| TiO ₂ NWs | 75 | 0.64 | 26 | 3.15 |
| 0.5% Au/TiO ₂ NWs | 46 | 0.43 | 34 | 3.11 |
| 3% Ag/TiO ₂ NWs | 48 | 0.49 | 32 | 3.13 |
| 2% Ag-0.5% Au/TiO ₂ NWs | 78 | 0.63 | 38 | 3.11 |

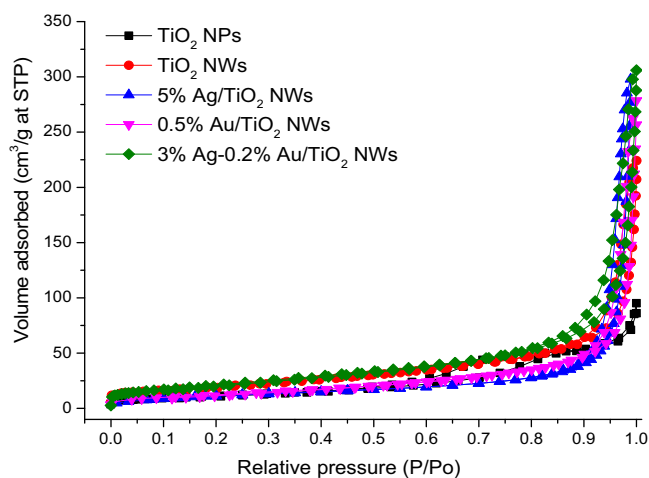


Fig. 5. N₂ adsorption-desorption isotherms of TiO₂ NPs, TiO₂ NWs and Au/Ag-deposited TiO₂ NWs samples.

of pore diameter, pure TiO₂ pore diameter was 10 nm, increased to 26 nm in TiO₂ NWs, apparently due to the larger diameter of TiO₂ NWs. A further increased in the pore diameter was observed in Au/Ag NPs loaded TiO₂ NWs seemingly due to deposited Au/Ag-NPs layer over the surface of these materials [31].

X-ray photo-electron spectroscopy (XPS) was used to analyze the chemical states of the elements in Au/Ag-NPs/TiO₂ NWs as shown in Fig. 6. The wide spectrum is presented in Fig. 6(a). Fig. 6(b) reveals the presence of Ti2p peaks namely Ti2p 3/2 and Ti2p 1/2, positioned at 458.08 and 463.72 eV which corresponds to Ti⁴⁺ or titanium dioxide (TiO₂). The Ag3d spectrum confirmed the presence of Ag in the metal state as depicted in Fig. 6(c) [21]. Fig. 6(d) presents Au 4f binding energy values of 82.03 eV (Au 4f_{7/2}) and 88.44 eV (Au 4f_{5/2}) in Au-Ag/TiO₂ NWs, attributed to metallic gold (Au⁰). Fig. 6(e) shows the O1s spectrum ascribed to the lattice oxygen O₂. This was also due to the presence of H₂O or the free hydroxyl group (O–H) on the TiO₂ surface. The spectrum of C 1s with peaks located at ~284.60 and 588.50 eV corresponds to C–C, and C=O, respectively as shown in Fig. 6(f).

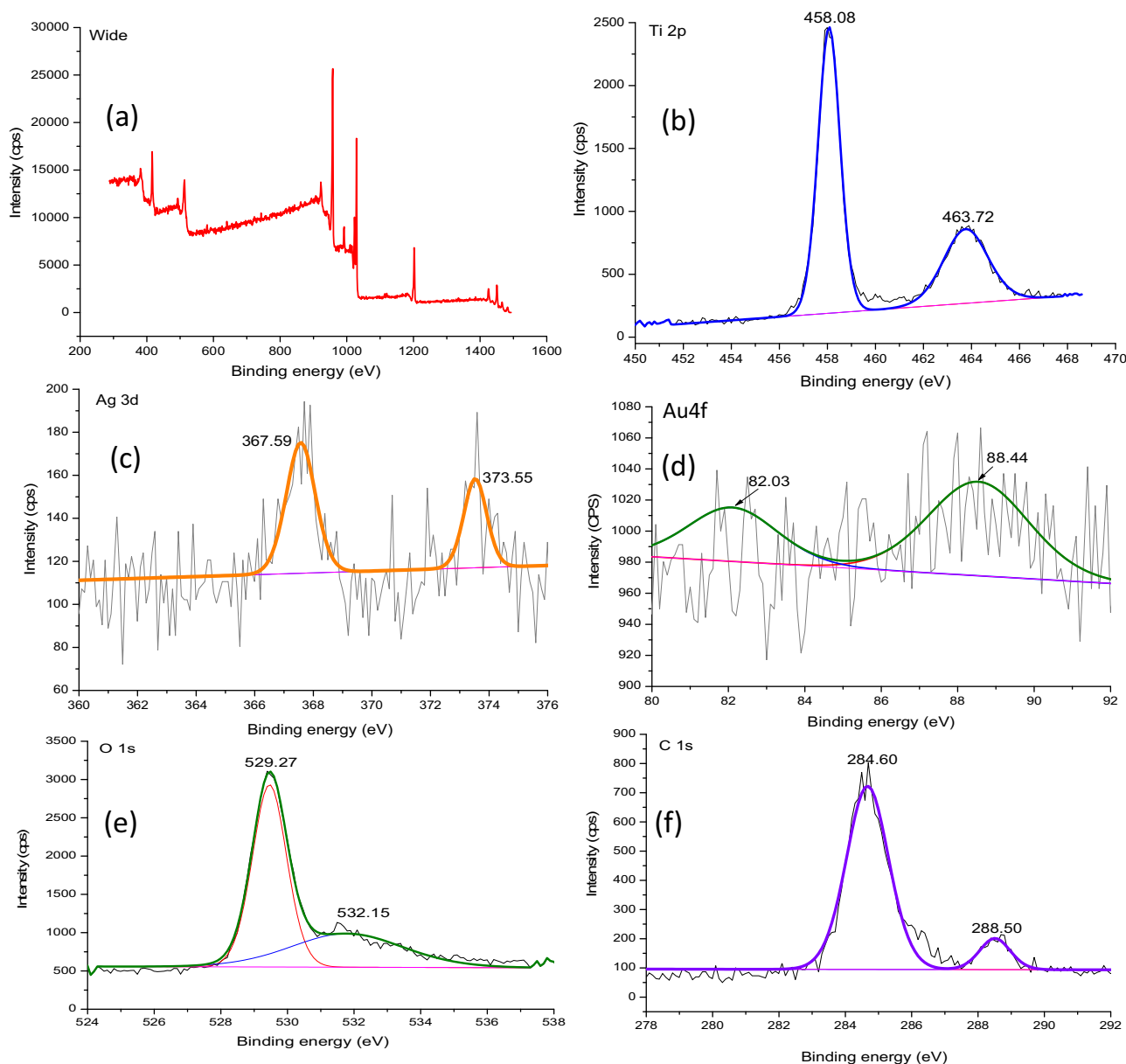


Fig. 6. XPS the spectra of 2 wt.% Ag–0.5 wt.% Au/TiO₂ NWs photocatalyst: (a) wide plot, (b) Ti 2p, (c) Ag-3d, (d) Au-4f, (e) O1s and C 1s.

The UV–vis diffuse reflectance absorbance spectra of the TiO₂ NWs and plasmonic Au/Ag loaded TiO₂ NWs samples are presented in Fig. 7(a). Both Au-NPs and Ag-NPs loaded into TiO₂ NWs revealed a broad visible light absorption peak due to LSPR absorption of Au-NPs and Ag-NPs, indicating metallic Au and Ag exists over the TiO₂ NWs surface as recognized by XPS. The LSPR peak of Ag-NPs appeared at 576 nm compared to its standard peak position of 450 nm. This red shift in peak toward longer wavelength was most likely due to the large size Ag-NPs with face centered cubic (fcc) structure of Ag [43–45]. However, Au-NPs give standard reflection with peak located at 580 nm due to LSPR of Au-NPs. On the other hand, the overlap between the plasmon resonance of 3% Ag–0.5% Au loaded TiO₂ NWs (around 450–700 nm) appeared and makes it difficult to see the individual response of both metals. The LSPR peak of Au/Ag NPs supported TiO₂ NWs was further broadened (around 410–750 nm) by loading 2% Ag and 0.5% Au into TiO₂ NWs. This, single broadened LSPR peak in the spectrum of Au/Ag NPs could probably be due to Au–Ag alloy formation, in good agreement with the previous reports [37,46]. More importantly, the illuminations

due to LSPR of Au/Ag NPs could be seen when the samples were excited with a laser beam of wavelength 532 nm, as depicted in Fig. 7(b–d). The emitting of light due to LSPR of Au and Ag NPs could be seen in Fig. 7(b–c). However, the obvious light glowing spots in the Au/Ag NPs co-coated TiO₂ NWs sample is evidently due to the Au–Ag alloy formation and less bright areas were due to the Au/Ag NPs co-coated over TiO₂ NWs as depicted in Fig. 7(d). These observations have confirmed the formation of Au–Ag alloy and gave strong LSPR response due to synergistic effect in Au/Ag metals.

Fig. 8 shows PL emission spectra of the pure TiO₂ NWs and Au/Ag-NPs modified TiO₂ NWs samples excited at a wavelength of 532 nm. The broad symmetric peaks appeared at 536 nm revealed that the emission is not because of TiO₂ band edge excitation [8]. Therefore, PL signals can be attributed to the transition of electrons from the oxygen vacancies to TiO₂ valance band. It is noticeable that emission spectra of the Au and Ag modified TiO₂ samples are similar to those of the pure TiO₂ NWs sample. However, the PL intensity enfeebled in Au-NPs and Ag-NPs sample and further reduced in

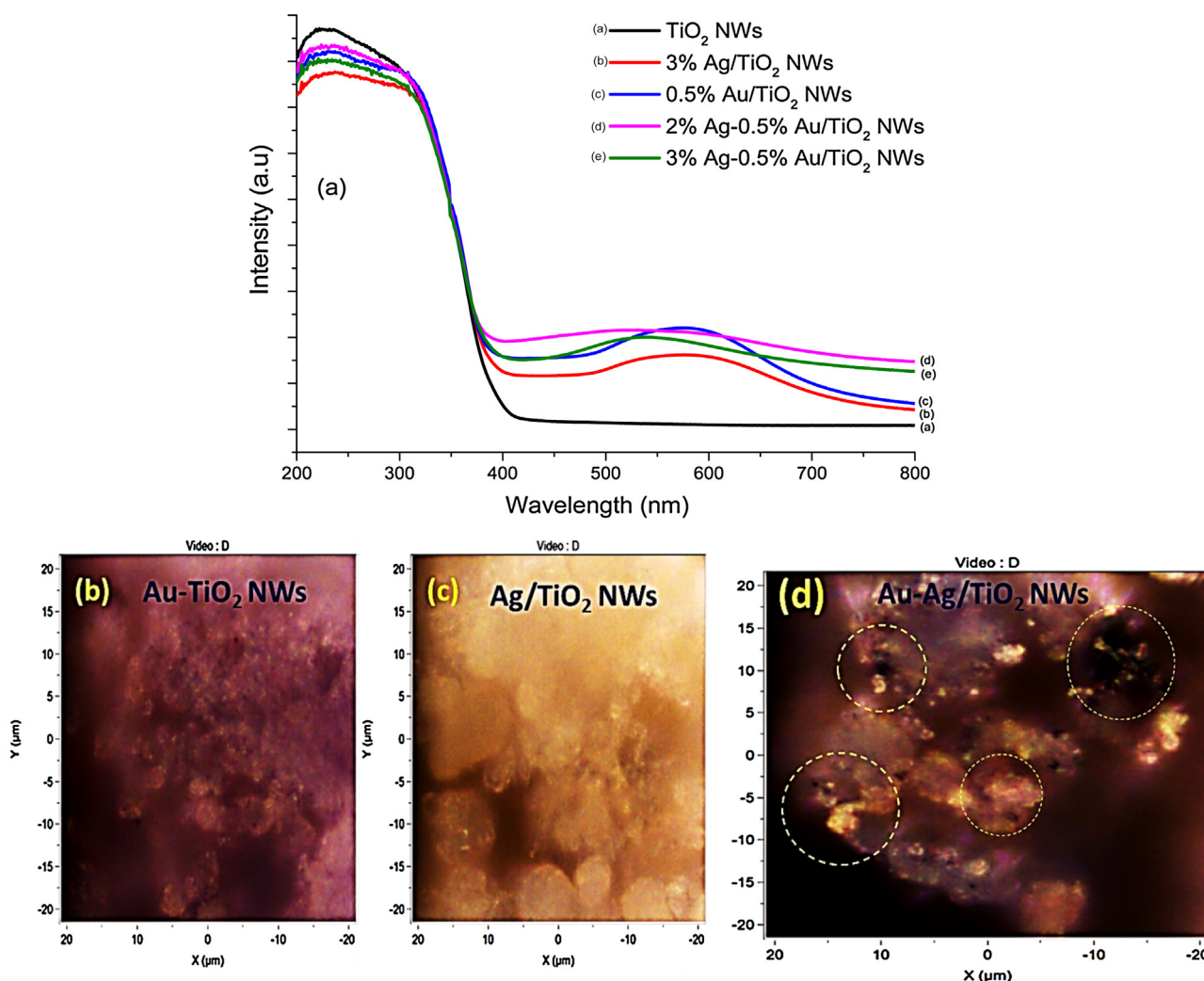


Fig. 7. (a) UV-vis diffuse reflectance absorbance spectra of TiO_2 NPs, TiO_2 NWs and Au/Ag-NPs loaded TiO_2 NWs, (b–d) Photographs of the illuminations of powder photocatalysts due to LSPR of Au/Ag NPs excited with a laser beam of wavelength 532 nm.

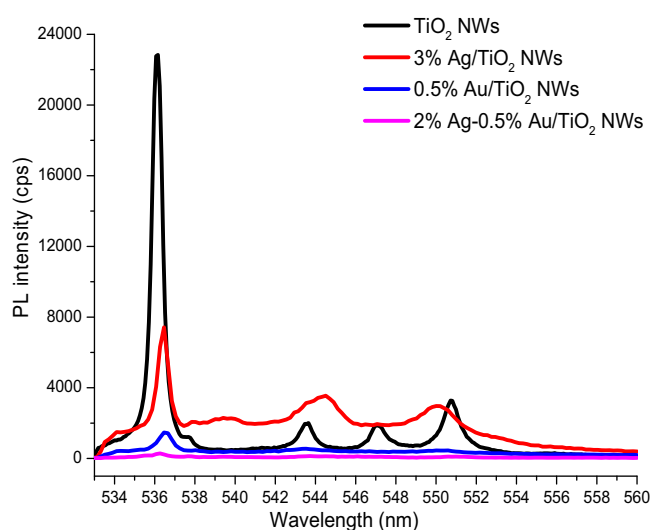


Fig. 8. Photoluminescence spectra of TiO_2 and Au/Ag NPs loaded TiO_2 samples.

Au/Ag NPs co-loaded TiO_2 NWs samples. The electron transfers from the TiO_2 NWs to Au/Ag promoted TiO_2 NWs are more effi-

cient than the single metal loaded TiO_2 NWs, confirming synergistic effects of these metals in TiO_2 NWs surface.

3.2. Photocatalytic CO_2 reduction with H_2

Prior to CO_2 photoreduction activity test, a series of preliminary tests were conducted in the absence of reductants (CO_2 , H_2) over all types of photocatalysts. In all cases, reaction products were not detected, confirming no organic residues in the catalyst. Additional preliminary tests were conducted using H_2 in presence of photocatalyst under light irradiations. Again, carbon containing compounds were not observed. However, a significant amount of CO was produced during CO_2 reduction with H_2 under the light irradiations in the presence of photocatalyst. These results have confirmed that the photoreduction products were obtained from the CO_2 source only. All the photocatalytic CO_2 reduction experiments were repeated at least in triplets and aggregated results have been reported.

The effects of Ag-NPs, Au-NPs and Au/Ag-NPs on the performance of TiO_2 NWs for photocatalytic CO_2 reduction with H_2 in the production of CO , CH_3OH and hydrocarbons under visible light irradiation are demonstrated in Figs. 9 and 10. Fig. 9 shows the effect of Ag-NPs and Au-NPs on the photoactivity of TiO_2 NWs for the production of CO as the main product with a smaller amount of hydrocarbons. We noted that in the absence of Ag/Au NPs, only

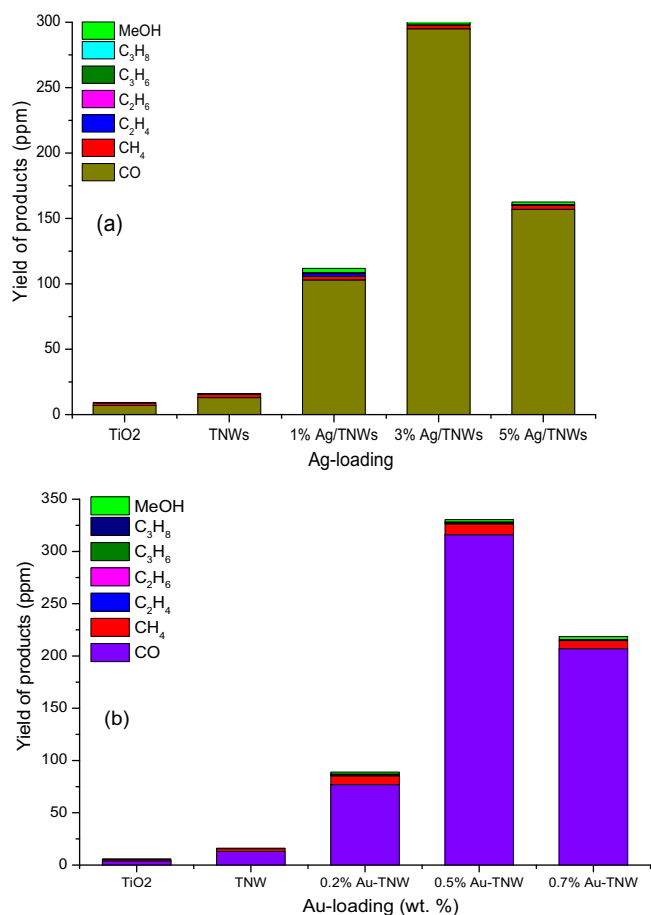


Fig. 9. Effect of Ag and Au NPs loading onto TiO₂ NWs photoactivity for CO, CH₃OH and hydrocarbons production during CO₂ reduction with H₂: (a) Ag-NPs loading, (b) Au-NPs loading.

smaller amount of CO was produced. However, a significant amount of CO production over TiO₂ NWs could be seen in the presence of Ag-NPs and Au-NPs. The pure TiO₂ and TiO₂ NWs have very low CO production because of their photoactivity only under the UV-light irradiations and perhaps due to fast recombination rate of photo-generated charge carrier. In contrast, Ag-NPs and Au-NPs decorated TiO₂ NWs exhibits much higher CO production rate with appreciable amounts of CH₃OH and hydrocarbons. This is because Ag-NPs and Au-NPs in TiO₂ NWs act as an electrons sink to suppress charges recombination rate. On the other hand, by contacting Ag-NPs and Au-NPs with TiO₂ NWs, the plasmon-excited electron can be injected into TiO₂ and makes it visible light active, while smaller size metal particles could serve as electron sink, resulting in prolonged recombination time. In this way, an immediate charges separation can be attained on the metal-semiconductor surface to enhance photoactivity. The optimal Ag-NPs and Au-NPs loading were found to be 3 wt.% and 0.5 wt.%, respectively, at which highest yield of products were detected. However, with higher metals-loading, the photoactivity was gradually reduced, possibly metals-NPs were adjacent to each other over TiO₂ NWs, creating recombination centers and electron-hole charges recombine immediately, resulting in lower photoactivity [21].

To evaluate the synergistic effects of Ag-NPs and Au-NPs, the TiO₂ NWs photoactivity was further evaluated in the presence of co-decorated Ag/Au NPs. The performance analysis of Au/Ag-NPs co-deposited on the TiO₂ NWs for photocatalytic CO₂ reduction with H₂ to CO is presented in Fig. 10(a). Interestingly, the CO production rate was remarkably enhanced using Au/Ag NPs co-loading

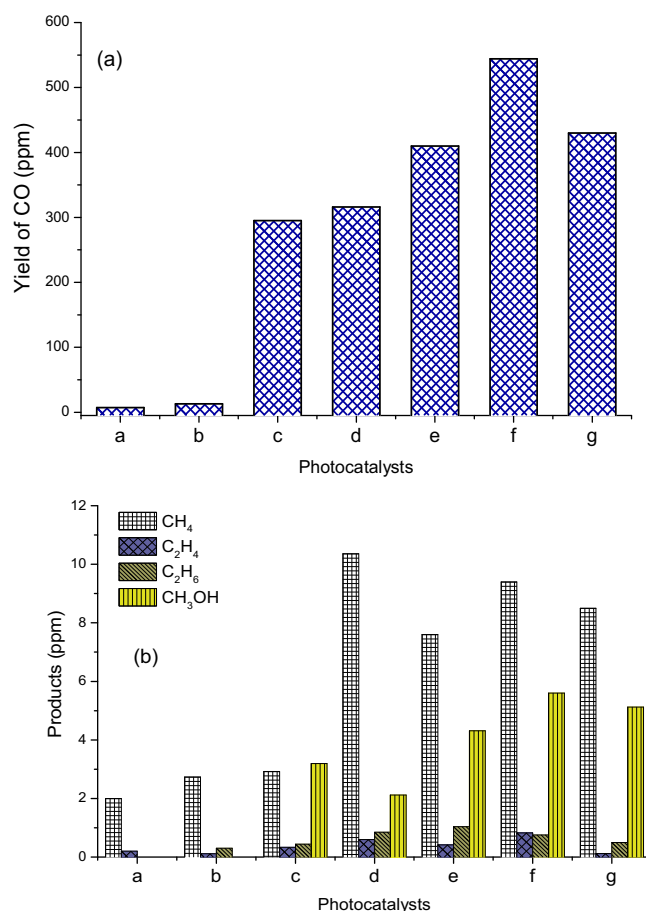


Fig. 10. Effect of Au/Ag-NPs co-loading onto TiO₂ photoactivity for CO and hydrocarbons production: (A) CO productions over photocatalysts (a) TiO₂, (b) TNWs, (c) 3% Ag-TNWs, (d) 0.5% Au-TNWs, (e) 1% Ag-0.5% Au/TNWs, (f) 2% Ag-0.5% Au/TNWs, (g) 3% Ag-0.5% Au/TNWs; (B) Methanol and hydrocarbons production over the corresponding photocatalysts.

as compared to Ag-NPs or Au-NPs. This suggests that synergistic effects, alloy formation optical responses (e.g. LSPR) and electrons sink of Au/Ag NPs over the TiO₂ NWs must play a crucial role in the production of CO and other products [35]. Evidently, all the Ag-NPs decorated Au-NPs/TiO₂ NWs photocatalysts demonstrated excellent performances for selective photoreduction of CO₂ to CO over the single metal-ions loaded TiO₂ NWs. The highest CO production was noticed over 2 wt.% Ag-NPs loaded into the fixed amount of 0.5 wt.% Au-NPs/TiO₂ NWs, which showed the optimal loading. It is noticeable to see that the optimal amount of Ag-NPs-loading in the pure TiO₂ NWs was 3 wt.%, while only 2 wt.% Ag-NPs loaded into 0.5 wt.% Au-NPs/TiO₂ NWs gave the optimal photoactivity. This revealed that Au/Ag NPs co-loading over the TiO₂ NWs significantly improved photoactivity toward CO evolution due to their synergistic effects.

The production of hydrocarbons and CH₃OH over Au/Ag NPs coated TiO₂ NWs are presented in Fig. 10(b). Using pure TiO₂ and TiO₂ NWs, production of CH₃OH was not detected, yet loading of both Au-NPs and Ag-NPs have favored production of CH₃OH and hydrocarbons. The production of CH₃OH was highest in the Au/Ag co-coated TiO₂ NWs samples, however, Au-NPs/TiO₂ NWs favored CH₄ production. Among the hydrocarbons, a significant amount of C₂H₆ was detected in the products mixture with appreciable amount of C₂H₄. The methanol and hydrocarbons production was significant using Au/Ag-NPs co-loading TiO₂ NWs samples, evidently due to Au-Ag alloy with absorption of broader light spectrum

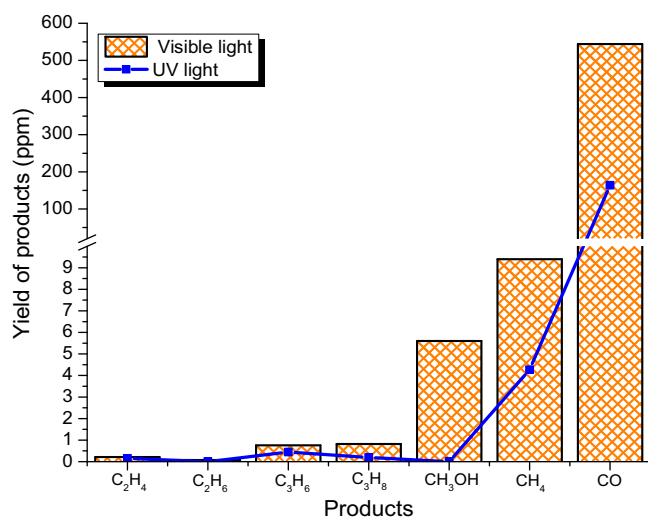


Fig. 11. Performance analysis of Au-Ag NPs supported TiO₂ NWs under UV and visible light irradiations.

and LSPR-excitation of TiO₂ NWs with electron sinks by these metals toward CO₂ reduction.

The effects of UV and visible light irradiations on the activity of plasmonic 2 wt.% Ag–0.5 wt.% Au-NPs loaded TiO₂ NWs for photo-induced CO₂ reduction to CO and hydrocarbons are demonstrated in Fig. 11. Obviously, the production of CO, CH₃OH and hydrocarbons was significant using visible-light-irradiations compared to UV-light under the same operating conditions. The amount of CO produced under visible-light was 3.28 fold more than using UV-light and similar trends could be seen for the production of hydrocarbons. More importantly, an appreciable amount of CH₃OH was also detected using visible light irradiations but was not detected with UV-light source. More importantly, the light intensity of UV-light (150 mW cm⁻²) was more stronger than the visible light irradiations (20 mW cm⁻²), yet the significantly enhanced photoactivity of Au/Ag NPs Co-loaded TiO₂ NWs toward CO₂ reduction was evidently due to synergistic effects between broad spectrum of visible light absorption by Au-Ag alloy and efficient electron separation by Au/Ag NPs.

The summary of yield rates and selectivity of different products over the various TiO₂ based catalysts during photocatalytic CO₂ reduction with H₂ as reducing agent under visible light irradiations are presented in Fig. 12 and tabulated in Table 2. The CO₂ reduction products observed were CO, CH₃OH, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ over different types of photocatalysts. The pure TiO₂ NPs and TiO₂ NWs show poor photoactivity for CH₃OH but found more efficient toward CO production. The photoactivity of CO₂ reduction was gradually increased using TiO₂ NWs than the TiO₂ NPs. This was conceivably due to effectual electron transfer over the TiO₂ NWs than the TiO₂ NPs. In comparison, the Au-NPs/TiO₂ NWs displays 1.07 times higher photoactivity for CO production than the Ag-NPs/TiO₂. This was because instead of LSPR function of Au-NPs, they are good electron acceptors to promote charges separation on the TiO₂ surface because of strong oxidation and reduction potentials in the Au-metal, as discussed in our previous work [47]. This was because of the higher electrons sink effect of the Au-NPs than the Ag-NPs due to its lower work function than the Ag-NPs, resulting in efficient separation of photo-generated charges. Therefore, multi-electron process would occur more efficiently over the Au-NPs than the Ag-NPs based TiO₂ NWs. However, the production of CO was significantly enhanced using Au/Ag NPs co-promoted TiO₂ NWs due to synergistic effects between Au-Ag alloy NPs, efficient visible light absorption, LSPR excitation of TiO₂ NWs, efficient

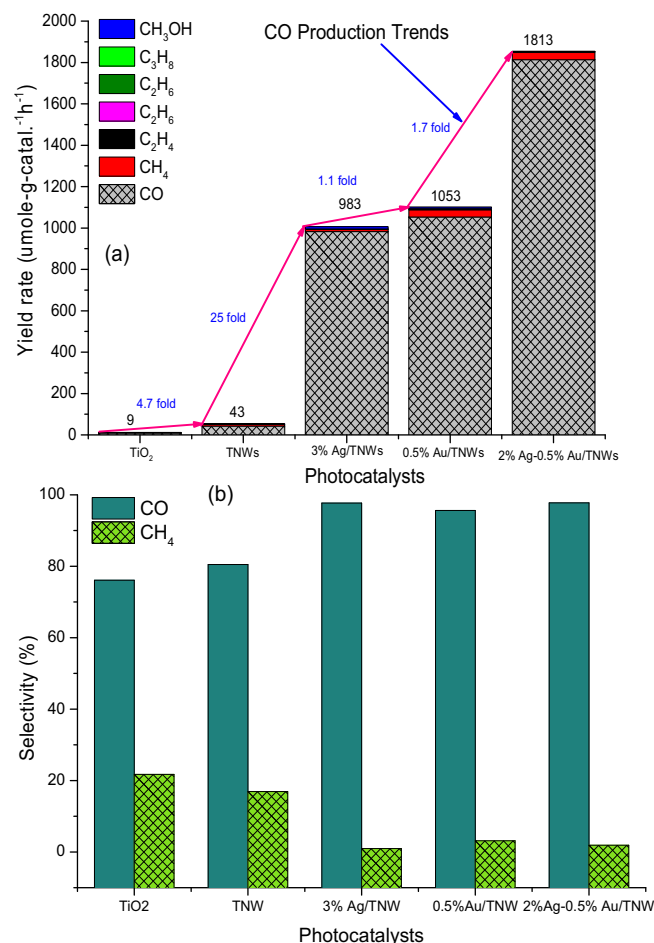


Fig. 12. (a) Yield rate of products over different photo-catalysts during CO₂ reduction with H₂; (b) Selectivity of CO and CH₄ for corresponding samples.

charge transfer property and hindered charges recombination rate by Au/Ag NPs.

The yield rate of CO over the Au/Ag-NPs loaded TiO₂ NWs was 1813 μmole g-catal.⁻¹ h⁻¹ which was higher than the Au-NPs/TiO₂ NWs (1053 μmole g-catal.⁻¹ h⁻¹), Ag-NPs/TiO₂ NWs (983 μmole g-catal.⁻¹ h⁻¹), TiO₂ NWs (43 μmole g-catal.⁻¹ h⁻¹) and un-doped TiO₂ (9 μmole g-catal.⁻¹ h⁻¹). This comparison demonstrated that the decoration of Ag/Au-NPs on the TiO₂ NWs structure enables great enhancement of photocatalytic efficiency through the LSPR-excitation of Au-Ag alloy or one of the metals (e.g. Au-NPs) and electron sink by the other metal (e.g. Ag-NPs), simultaneously. The yield rate of CH₄ production was higher in the order of Au/Ag/TiO₂ NWs > Au/TiO₂ NWs > Ag/TiO₂ NWs > TiO₂ NWs > TiO₂. The CH₃OH production was detected only over Au-NPs and Ag-NPs loaded TiO₂ NWs. However, much higher CO production over Au/Ag-NPs/TiO₂ NWs was obviously due to higher electron mobility with hindered recombination rate and LSPR effect of Au/Ag-NPs. The selectivity for CO production over TiO₂ NWs was 80%, increased to 97% in Au/Ag-NPs co-loaded TiO₂ NWs. This increased in selectivity was due to efficient photo-induced CO₂ to CO conversion over plasmonic Au/Ag NPs promoted TiO₂ catalysts. These observations have confirmed that the RWGS reaction is favorable for CO₂ reduction by H₂ to CO due to LSPR of Au/Ag NPs in TiO₂ NWs [13,47]. Furthermore, stability and reusability test of Au/Ag-NPs co-deposited TiO₂ NWs for photocatalytic CO₂ reduction with H₂ through a cycling run was conducted. There was no obvious decrease of the photoactivity of Au/Ag-NPs-loaded TiO₂ after three cyclic runs, demonstrating the good stability of this photo-catalyst.

Table 2
Summary of yield rate of CO₂ photo-reduction over TiO₂, TiO₂ NW and Au/Ag-deposited TiO₂ NWs photocatalysts.

| Catalysts | Production rate ($\mu\text{mole g-catal.}^{-1} \text{ h}^{-1}$) | | | | | | | Selectivity (%) | |
|------------------------------------|--|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------|-----------------|-----------------|
| | CO | CH ₄ | C ₂ H ₄ | C ₂ H ₆ | C ₃ H ₆ | C ₃ H ₈ | CH ₃ OH | CO | CH ₄ |
| TiO ₂ | 9 | 3.0 | 0.27 | – | – | – | – | 76.09 | 21.74 |
| TiO ₂ NWs | 43 | 9 | 0.38 | 1.01 | – | – | – | 80.50 | 16.93 |
| 0.5% Au-NPs/TiO ₂ NWs | 1053 | 30 | 1.99 | 2.83 | 0.44 | 1.23 | 7.07 | 95.63 | 3.14 |
| 3% Ag-NPs/TiO ₂ NWs | 983 | 10 | 1.11 | 1.48 | 0.23 | 1.12 | 10.65 | 97.72 | 0.97 |
| 2% Ag–0.5% Au–TiO ₂ NWs | 1813 | 35 | 0.95 | 2.52 | 3.94 | 3.52 | 18.76 | 97.70 | 1.86 |

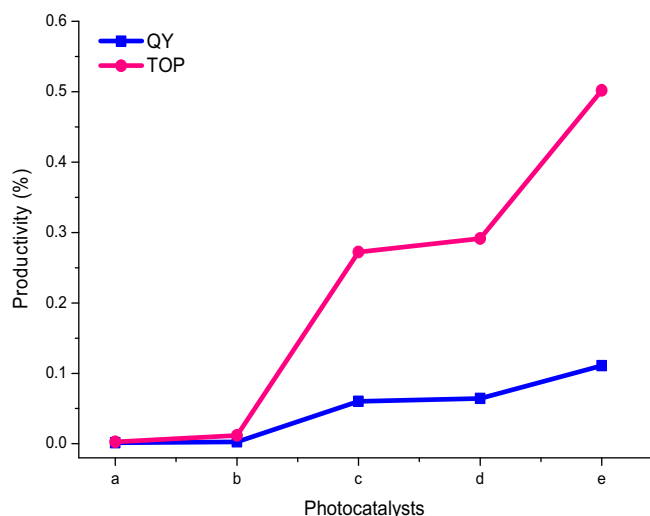


Fig. 13. Plot of quantum yield and turn over productivity for CO production over different photo-catalysts: (a) TiO₂, (b) TiO₂ NWs, (c) 3% Ag/TiO₂ NWs, (d) 0.5% Au/TiO₂ NWs, (e) 2% Ag–0.5% Au/TiO₂ NWs.

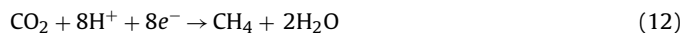
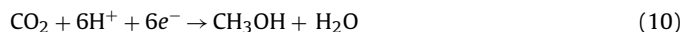
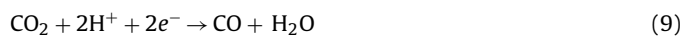
It is generally accepted that the photocatalyst efficiency is mainly dependent on the light absorption ability, surface properties (e.g., specific surface area, pore structure, pore volume, adsorption property etc.) and photo-generated electron/hole pairs separation efficiency. It is evidenced that photoactivity for CO evolution rate over the TiO₂ NWs can be improved by 23 fold over 3 wt.% Ag-NPs loading and 25 fold by 0.5 wt.% Au-loading. However, as discussed above the TiO₂ NWs surface area is much higher than the Au-NPs and Ag-NPs loaded TiO₂ NWs, indicating that in the current study, this factor is not crucial to the photocatalytic activity for Au-NPs and Ag-NPs/TiO₂ NWs. The enhanced photocatalytic activity can be mainly attributed to surface plasmon resonance of Au-NPs and Ag-NPs. More importantly, the surface area of TiO₂ NWs and Au–Ag-NPs/TiO₂ NWs are much closer, yet CO production rate over 2 wt.% Ag–0.5 wt.% Au-co-loading TiO₂ NWs was 42 fold more than the amount produced over the pure TiO₂ NWs. Therefore, this significantly enhanced photocatalytic activity of Au/Ag NPs co-coated TiO₂ NWs mainly attributed to strong visible light absorption due to surface plasmon resonance of Au–Ag alloy and synergistic effect between Au/Ag-NPs. This can greatly promote the production and separation of photo-generated carriers under the broader visible light spectrum.

The quantum yield was calculated based on 2 electrons used for CO production and moles of photons input energy over the catalyst surface. The quantum yields (QY) and turn over productivity (TOP) of CO over TiO₂ NWs and Au/Ag-NPs loaded are shown in Fig. 13 and summarized in Table 3. The significantly enhanced QY could be seen over Au/Ag-NPs/TiO₂ NWs compared to Au-NPs/TiO₂ NWs, Ag-NPs/TiO₂ NWs and pure TiO₂ NWs. More importantly, TOP was more significant over Au/Ag NPs loaded TiO₂ NWs compared to single-metal loaded TiO₂ NWs and bare TiO₂ NWs. This was evidently due to efficient charge transfer rate and SPR-excitation due

to synergistic effect of Au/Ag-NPs. It is evident that TOP is much higher than QY because it was calculated based on the operating parameters. The pressure has positive effects on TOP but reduced with increase of temperature and catalyst loading. However, QY is independent of these operating parameters which are very important in photocatalysis system. In different research work, results were reported at different catalyst loading and reaction temperature, yet the results were compared based on QY. Therefore, the performance of the photocatalytic system in gas phase system could be accurately compared based on TOP than the QY.

3.3. The mechanism of photocatalytic reaction

LSPR-induced photocatalytic reaction mechanism of TiO₂ loaded with metal-NPs has been discussed in several reports [31,35]. The visible light can provide an energy transfer channel while the light captured by TiO₂ NWs can be reused by Au-NPs resulting in enhanced LSPR effect. The LSPR-excitation of Au/Ag-NPs enhances visible light excitation through strong localized electric field and improves charge separation on TiO₂ NWs [48]. Electrons can be injected from LSPR-excited by Au–Ag alloy or Au/Ag NPs toward TiO₂ surface, captured by Au/Ag-NPs and subsequent reduction and oxidation reactions occur for CO₂ and H₂, respectively. This synergetic effect in Au/Ag NPs over TiO₂ NWs for LSPR-induced chemical reaction has been proposed as for the reaction mechanism. The overall proposed mechanism to understand the reaction process is illustrated in Eqs. (3)–(12) [22].



On the basis of above results and discussion, CO₂ reduction and H₂ oxidation over Au/Ag-NPs supported TiO₂ NWs can be explained as follows: First, when the visible light was irradiated to Au/Ag-NPs/TiO₂ NWs, photons were absorbed by the Au/Ag NPs due to the LSPR excitation as explained in Eqs. (3) and (4). The excited electrons in the Au/Ag are injected into the conduction band of TiO₂ (Eq. (5)). The electrons are transferred toward Au/Ag metals, making them to react easily with CO₂ as illustrated in Eqs. (6)–(7). The valence band holes are used to oxidize H₂ for the production of hydrogen radicals (Eq. (8)). Then, H⁺ radicals and active electrons can reduce CO₂ to CO, CH₃OH and CH₄ as explained in Eqs. (9)–(11). CO production needs only two electrons and two protons (Eq. (9)).

Table 3
Summary of QY and TOP of CO production over various photocatalysts.

| Catalysts | Yield of CO ($\mu\text{mole g-catal.}^{-1} \text{ h}^{-1}$) | QY (%) | TOP (%) |
|------------------------------------|---|--------|---------|
| TiO ₂ | 9 | 0.0014 | 0.0025 |
| TiO ₂ NWs | 43 | 0.0026 | 0.0119 |
| 3% Ag-TiO ₂ NWs | 983 | 0.0601 | 0.2721 |
| 0.5% Au-TiO ₂ NWs | 1053 | 0.0643 | 0.2915 |
| 2% Ag–0.5% Au-TiO ₂ NWs | 1813 | 0.1108 | 0.5018 |

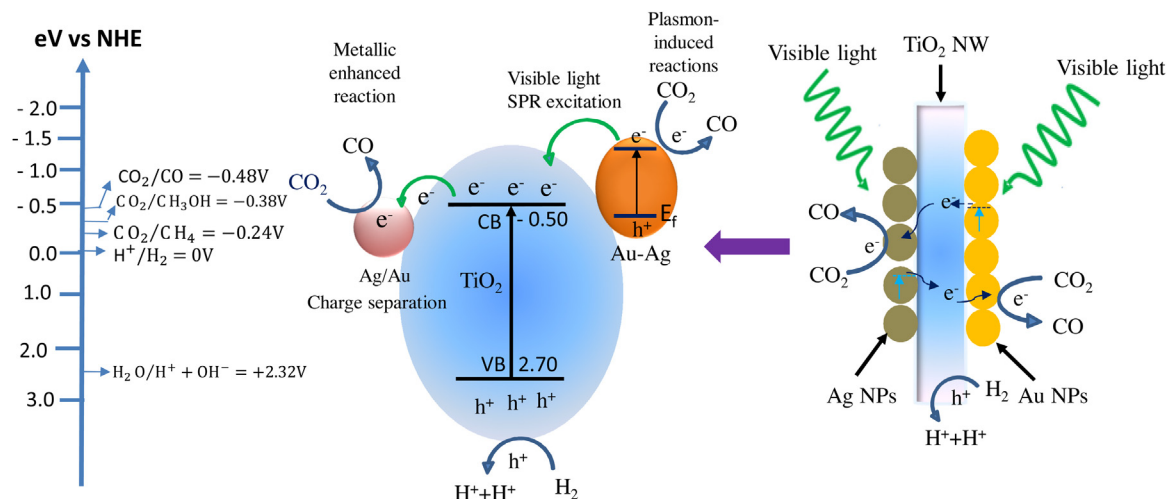


Fig. 14. Proposed mechanism showing a photocatalytic process for CO₂ reduction by H₂ to CO on Au/Ag-NPs/TiO₂ NWs under visible light irradiation.

The production of CO as the main product was due to the proximity of thermodynamic difference between TiO₂ CB (−0.5 eV) and the reduction potential of CO₂/CO (−0.48 eV). CH₃OH and CH₄ can be produced directly through a multi-step reduction process which involved six and eight electrons and protons, respectively (Eqs. (10) and (12)). Besides, there would also be possible production of CH₄ by the depletion of as-produced CO through a six electron reaction involvement (Eq. (11)). Therefore, significantly enhanced photocatalytic activity by Au/Ag-decorated TiO₂ NWs can be explained based on synergistic effects and LSPR excitation.

The schematic presentation of plasmon-enhanced photocatalytic activity over the Au/Ag NPs co-promoted TiO₂ NWs is illustrated in Fig. 14. Upon LSPR excitation, the surface electron on Au/Ag NPs or Au–Ag alloy can be excited to a higher energy level where electrons are transferred to CB band of TiO₂ NWs through metals–TiO₂ NWs interfaces. At the same time, electron-hole separation of photo-excited TiO₂ may be promoted by smaller size Au/Ag NPs, which serves as electron sink and allows a longer lifetime of photo-generated electrons. In conclusions, the overall high photocatalytic activity of Au/Ag-NPs loaded TiO₂ NWs in solar fuels production can be attributed to efficient visible light absorption by Au–Ag alloy NPs, synergistic effects of LSPR excitation and electron sink of Au/Ag NPs.

4. Conclusions

Au/Ag-NPs-co-decorated TiO₂ NWs have been successfully fabricated using a facile thermal and photo-deposition method. Plasmon-induced photocatalytic CO₂ reduction by H₂ over Au/Ag NPs-co-decorated TiO₂ NWs were successfully conducted under visible light irradiation. The photo-activity of Au-NPs/TiO₂ NWs was more than Ag-NPs/TiO₂ NWs, probably due to greater LSPR effects by Au-NPs. The Au/Ag NPs loaded onto TiO₂ NWs exhibited remarkably improved visible light photocatalytic activity for CO evolution as compared to TiO₂ NWs with only single metal deposition (Au-NPs/TiO₂ NWs and Ag-NPs/TiO₂ NWs). CO evolution rate

of Au/Ag-NPs/TiO₂ NWs was approximately 72.52 times more than the amount produced over the pure TiO₂ NWs. The amount of CO produced under visible-light was 3.28 fold more than the amount produced using UV-light irradiations. These enhanced photocatalytic activities through co-deposition of Au/Ag NPs are attributed to synergistic effects based on LSPR excitation and electrons sink of Au/Ag NPs. The turnover productivity revealed, operating parameters have great influences to improve photoactivity and products selectivity. Therefore, synergistic effect between charger transfer and placement-excitation of Au/Ag-NPs can greatly enhance the performance of TiO₂ NWs. Thus, co-deposition of plasmonic Au–Ag alloy and Au/Ag NPs could provide a more effective way to harvest solar energy over a broader range of solar spectrum.

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